

Manufacturing Nanocrystalline Materials by Physical Vapor Synthesis

By Quinton Ford, Director of Marketing, Industrial Products,
Nanophase Technologies Corp., Burr Ridge, Ill.

A CONTINUOUS PROCESS BASED ON GAS-PHASE CONDENSATION CAN PRODUCE NANOCRYSTALLINE PARTICLES IN ECONOMICAL QUANTITIES.

During the past decade, a great deal of research and development has been focused on fabricating and characterizing nanocrystalline materials. Within the industry, nanocrystalline materials are commonly defined as crystalline materials that have an average particle or grain size of less than 100 nanometers (0.1 micron). A deliberate distinction is made between nanocrystalline materials and submicron crystalline materials, which have an average particle or grain size of less than 1 micron.

The relative percentage of interfacial atoms to total atoms in a material increases dramatically with decreasing size below 100 nanometers (see Figure 1). The resultant properties of nanocrystalline materials thus have a much greater dependence on the contributions of interfacial atoms (those atoms on the surface of a particle or in the grain boundaries of a consolidated material) than submicron materials. Some unconventional mechanical, chemical, electrical, optical and magnetic properties exhibited by nanocrystalline materials are attributed to this greater dependence on the contributions of interfacial atoms.

PROCESSING METHODS

A wide range of techniques have been developed to fabricate nanocrystalline materials. The most commonly practiced of these are gas-phase condensation, sol-gel chemistry, spray pyrolysis and hydrothermal processing. The challenge with all techniques is to successfully scale

production to commercial volumes of nanocrystalline materials with properties and economies that allow their use in mainstream applications. One of the first techniques to be so scaled, physical vapor synthesis, is based on the principles of gas-phase condensation.

In the 1980s, gas-phase condensation was demonstrated to be capable of fabricating a wide range of ceramic and metallic nanocrystalline particles. Gas-phase condensation involves the evaporation of precursor materials in reduced-pressure, inert environments. After evacuating a chamber, inert gas is introduced to create the reduced-pressure environment. The

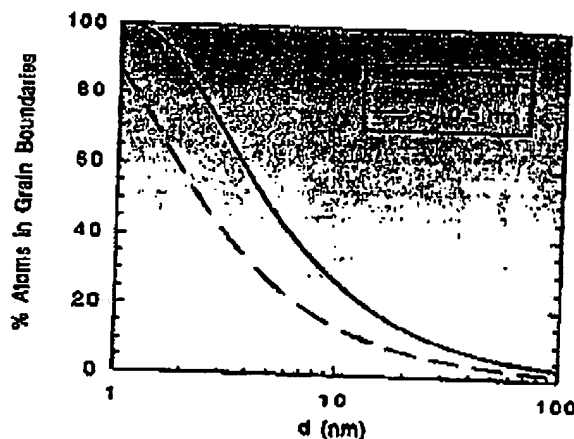
precursor material is then evaporated using any of a variety of energy sources.

Atoms of evaporated precursor collide with the cooler atoms of the inert backfill gas. These cooler gas atoms cause the evaporated precursor to condense and solidify as nanocrystalline particles of the precursor. If reactive gas is used for backfill instead of inert gas, the evaporated precursor and gas react, condense and solidify as nanocrystalline particles of the formed compound.

The cooling of the gas is caused by convective currents that are created within the chamber by the temperature gradient between the energy source and a

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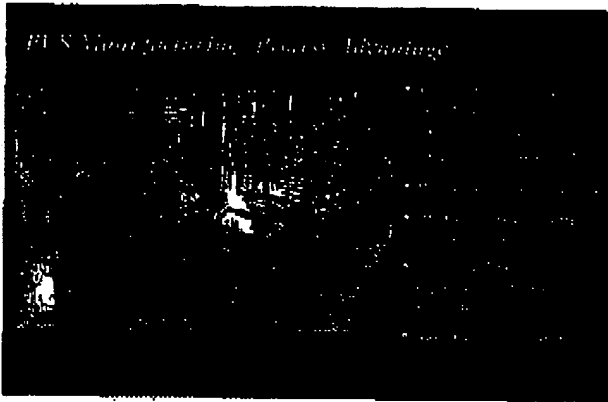
Figure 1



Percentage of atoms in grain boundaries of nanocrystalline material as a function of average grain size assuming grain boundary thickness range of 0.5 to 1 nanometer. (From R.W. Siegel, "Cluster-Assembled Nanophase Materials", *Annu. Rev. Mater. Sci.* 21, 659-678, 1991)

Nanocrystalline Materials

Figure 2



A bay of physical vapor synthesis production machines is readied.

Figure 3



Schematic of the physical vapor synthesis technique.

Using Physical Vapor Synthesis Materials in Polishing Slurries

One commercial application of physical vapor synthesis materials is as an abrasive component for polishing slurries used in the production of semiconductors. Current trends in semiconductor design include decreasing line widths and increasing numbers of metal and dielectric layers. These design trends present significant issues during photolithography steps unless the layers to be imaged are planar across the entire wafer. A process referred to as chemical mechanical planarization (CMP) is gaining widespread acceptance within the industry to polish the sputtered metal and dielectric layers on the semiconductor wafers to a highly planar state.

Aluminum oxide produced by physical vapor synthesis is incorporated into slurry for planarizing tungsten metal layers. The slurry is prepared by introducing the aluminum oxide powder to water, adding mechanical energy to break down agglomerates, and extracting particles comprising the upper end of the particle size distribution. Oxidizing chemicals are later blended with the abrasive slurry just prior to use.

Slurry containing aluminum oxide produced by physical vapor synthesis has been evaluated as superior to other slurries in defectivity and microscratching of tungsten surfaces. The concurrent removal rates and uniformities are comparable to those of other slurries. Consequently, cost of ownership can be lowered by the overall performance of slurry containing physical vapor synthesis aluminum oxide.

Cerium oxide produced by physical vapor synthesis is currently being evaluated as an additive to slurries for planarization of dielectric layers. Such slurries generally contain silica as the sole abrasive component. Initial tests indicate that adding a small percentage of cerium oxide to silica-based slurries can increase removal rates to four times the rates of slurries containing no cerium oxide. No concurrent degradation of defectivity, microscratching or uniformity have been detected.

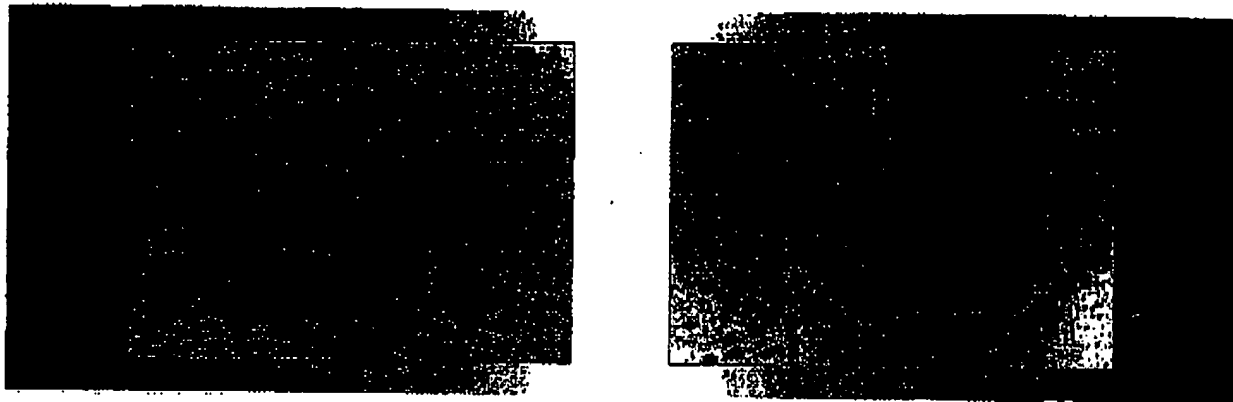
cooled collection surface. These convective currents carry the nanocrystalline particles to the collection surface, where they are later harvested. The collection surface is typically the outer surface of a metal tube through which liquid nitrogen is passed.

IMPROVING OUTPUT

Nanocrystalline particles produced via gas-phase condensation are equiaxed, nonporous, free of residual surface chemicals, and have a narrow particle size distribution. However, the reduced-pressure conditions and dependence on natural convection limit the technique to a low-rate batch process. Practically-sized systems can produce only tens of grams of nanocrystalline materials per day, resulting in economies that are not feasible for most applications.

In the early 1990s, scientists at Nanophase Technologies developed a patented technique based on the principles of gas-phase condensation. This technique produces particles with similar attributes to those produced through gas-phase condensation, while eliminating the need for reduced-pressure conditions and the dependence on natural convection. The technique, named physical vapor synthesis, operates as a continuous process and at significantly increased rates compared to gas phase condensation.

A single physical vapor synthesis production machine is capable of delivering tens of kilograms of nanocrystalline materials per day. This provides economies that are feasible for a large

Figure 4

Transmission electron microscopy of yttrium oxide (left) and aluminum oxide (right) produced by physical vapor synthesis.

number of applications. The technique has already been successfully scaled to a production capacity exceeding 100 tons per year, and additional capacity can be added in a modular fashion as needed (see Figure 2).

COOLING REQUIRED

In physical vapor synthesis (Figure 3), precursor material is introduced at a controlled rate into a chamber. Within the chamber, a plasma arc is formed between a nonconsumable electrode and the consumable precursor. The precursor, typically a high-purity metal rod, passes through the plasma arc and is melted and vaporized.

A quench and/or reactive gas is introduced to the chamber. Atoms of evaporated precursor collide with the cooler atoms of the quench gas. The evaporated precursor condenses and solidifies as nanocrystalline particles of the precursor. If a reactive gas is also present, it reacts with the evaporated precursor, causing nanocrystalline particles of the resultant compound to be formed upon condensation and solidification.

After the nanocrystalline particles are solidified, their temperature is still elevated. The particles must be cooled to minimize agglomeration. Additional gas is turbulently introduced to accelerate cooling of the particles. The gas propels the particles into a collector housing. The collector housing contains filter media that allows the gas to exit but traps the weakly agglomerated nanocrystalline particles. The nanocrystalline particles

Advantages of Physical Vapor Synthesis

- ◆ Economical
- ◆ Narrow particle size distribution
- ◆ Continuous process
- ◆ Particle size control
- ◆ Nonporous, equiaxed particles
- ◆ High-purity materials
- ◆ Wide range of oxides

collect on the filter media in the collector housing and are periodically harvested.

PRODUCT CHARACTERISTICS

Numerous nanocrystalline oxides and noble metals have been successfully fabricated using physical vapor synthesis. These include aluminum oxide, titanium dioxide, zinc oxide, iron oxide, cerium oxide, yttrium oxide, copper oxide, magnesium oxide, manganese oxide, indium oxide, palladium, silver, gold and platinum.

Non-noble metals are also of commercial interest in nanocrystalline form. However, in this size regime, the surfaces of these particles are highly reactive and will oxidize when exposed to air. In the case of some metals, this oxidation causes violent combustion. Several methods to stabilize particles are under development and are expected to allow eventual commercialization of these metals. Additionally, fabrication of such materi-

als as nanocrystalline carbides and nitrides will be attempted with modifications to the current physical vapor synthesis practices.

A metastable phase of a material generally results from physical vapor synthesis due to the high process temperatures and rapid solidification. Particle morphologies vary with material, although they are commonly equiaxed. Aluminum oxide particles produced appear perfectly spherical when imaged by SEM or TEM (see Figure 4).

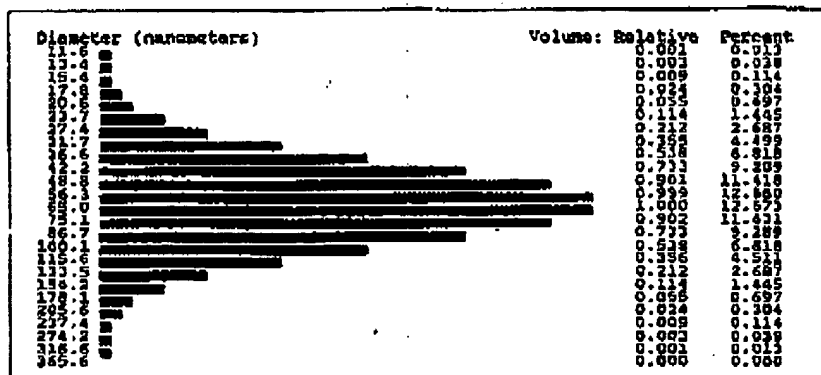
PARTICLE SIZE CONTROL

Physical vapor synthesis provides sufficient control to allow concurrent adjustment of the specific surface area and the average particle size of production materials. Specific surface areas can be varied from approximately 30 to 90 m²/g as desired. This corresponds to average particle sizes ranging from approximately 10 to 100 nanometers. Based on close correlation between average particle sizes measured from TEM images and calculated from BET specific surface areas, physical vapor synthesis particles are virtually nonporous.

More important than the average particle size in most applications is the particle size distribution, specifically the upper end of the distribution. Physical vapor synthesis materials have lognormal distributions, with one endpoint at a few nanometers and another between 300 and 500 nanometers (see Figure 5). Less than 1% of the particles are above 150 nanometers.

Nanocrystalline Materials

Figure 5



Volume-weighted particle size distribution of aluminum oxide produced by physical vapor synthesis.

When the particles are collected from physical vapor synthesis, they are weakly agglomerated up to tens of microns. The agglomerates can be broken down to the particle size distributions described above by such techniques as ultrasonication and

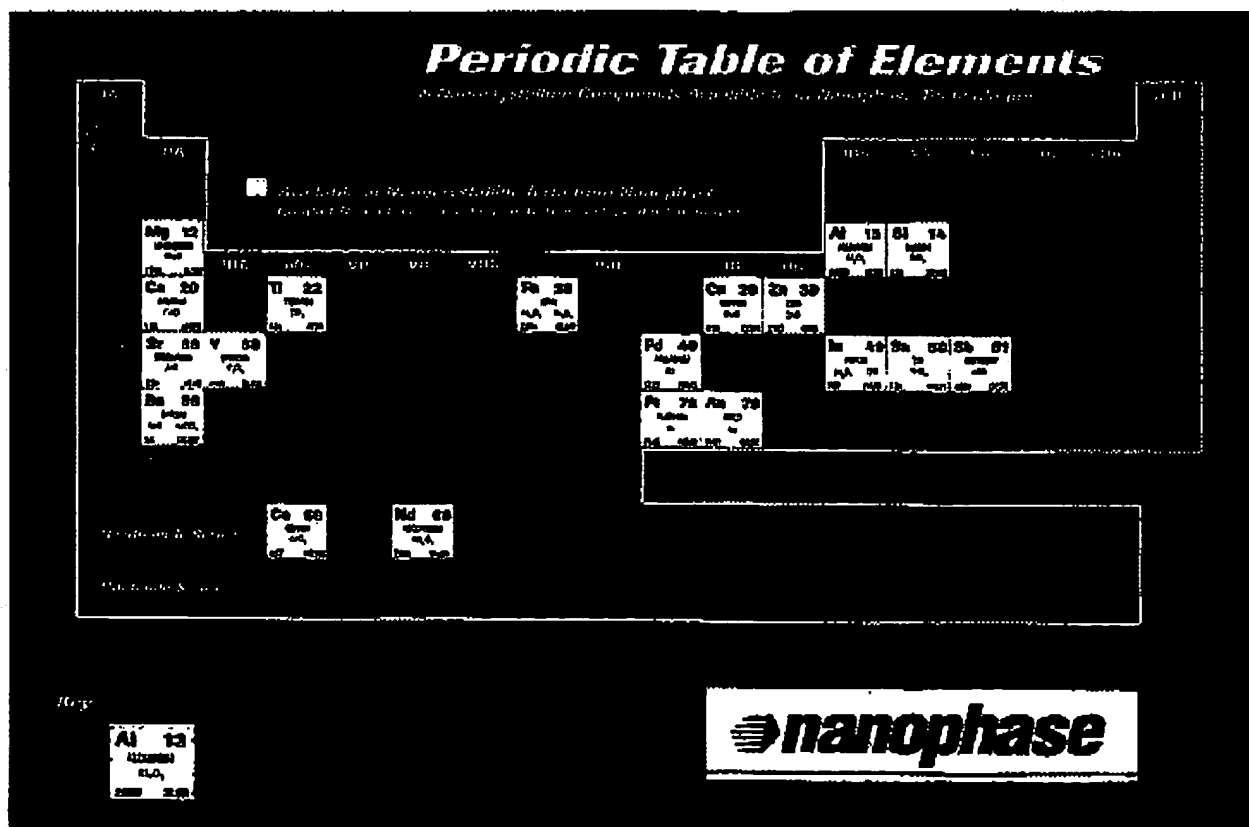
media milling. Further refinement of these particle size distributions is also possible, eliminating particles above a specific size.

The overall purity of physical vapor synthesis nanocrystalline particles

approximates the purity of the precursor material. Consequently, precursors commensurate with the overall purity requirements of the application are used. Specific impurities of concern for a given application can be engineered to desired levels.

APPLICATIONS

Applications for oxide particles produced by physical vapor synthesis have already been commercialized and include abrasives in polishing slurries for semiconductors, anti-fungal agents for health care and additives to increase the wear resistance of polymers. Additional applications for oxide and noble metal particles are also being developed. These include transparent conductive coatings, precious metal catalysts and additives to provide various functionalities to polymers. □



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